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14. ABSTRACT <p>Kapton[®] is used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. Atomic oxygen (AO) in low Earth orbit (LEO) causes severe degradation of Kapton[®]. SiO₂ coatings impart remarkable oxidation resistance to Kapton[®], yet imperfections in the SiO₂ application process and micrometeoroid / debris impact in orbit damage the SiO₂ coating leading to Kapton[®] erosion.</p> <p>Polyhedral oligomeric silsesquioxane (POSS) is a silicon and oxygen cage-like structure surrounded by organic groups which can be polymerizable. POSS-diamine was polymerized with the Kapton[®] monomers, pyromellitic dianhydride and 4,4'-oxydianiline. The resulting POSS-Kapton[®] polyimide (PI) is self-passivating by the formation of a silica layer upon exposure to AO. Evidence of a SiO₂ passivation layer has been shown by X-Ray Photoelectron Spectroscopy studies on AO exposed samples, and erosion yields of 3.5, 7.0, and 8.75 weight % Si₈O₁₁ MC-POSS-PI samples which were 3.7, 0.98, and 0.3 percent, respectively, of the erosion yield for Kapton H[®] at a fluence of 8.5 x 10²⁰ O atoms cm⁻².</p> <p>The self-passivation of POSS-Kapton[®]-PIs has also been demonstrated by monitoring a 1 micron deep scratch in MC-POSS-PI after exposure to AO. Kapton H[®], SiO₂ coated Kapton HN[®] and 8.75 wt % Si₈O₁₁ MC-POSS-PI samples were exposed to AO, scratched, and re-exposed to AO. Upon the first exposure, these samples eroded 5.0 µm, 0 µm, and 200 nm respectively. Upon the second exposure the samples eroded, respectively, an additional 5.0 µm within and outside of the scratch, and 7.0 µm and 200 nm within the scratch only.</p>					
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Comparisons of Polyhedral Oligomeric Silsesquioxane (POSS) Polyimides as Space-Survivable Materials

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ABSTRACT

Kapton[®] is used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. Atomic oxygen (AO) in low Earth orbit (LEO) causes severe degradation of Kapton[®]. SiO₂ coatings impart remarkable oxidation resistance to Kapton[®], yet imperfections in the SiO₂ application process and micrometeoroid / debris impact in orbit damage the SiO₂ coating leading to Kapton[®] erosion.

Polyhedral oligomeric silsesquioxane (POSS) is a silicon and oxygen cage-like structure surrounded by organic groups which can be polymerizable. POSS-diamine was polymerized with the Kapton[®] monomers, pyromellitic dianhydride and 4,4'-oxydianiline. The resulting POSS-Kapton[®] polyimide (PI) is self-passivating by the formation of a silica layer upon exposure to AO. Evidence of a SiO₂ passivation layer has been shown by X-Ray Photoelectron Spectroscopy studies on AO exposed samples, and erosion yields of 3.5, 7.0, and 8.75 weight % Si₈O₁₁ MC-POSS-PI samples which were 3.7, 0.98, and 0.3 percent, respectively, of the erosion yield for Kapton H[®] at a fluence of 8.5×10^{20} O atoms cm⁻².

The self-passivation of POSS-Kapton[®]-PIs has also been demonstrated by monitoring a 1 micron deep scratch in MC-POSS-PI after exposure to AO. Kapton H[®], SiO₂ coated Kapton HN[®] and 8.75 wt % Si₈O₁₁ MC-POSS-PI samples were exposed to AO, scratched, and re-exposed to AO. Upon the first exposure, these samples eroded 5.0 μm, 0 μm, and 200 nm respectively. Upon the second exposure the samples eroded, respectively, an additional 5.0 μm within and outside of the scratch, and 7.0 μm and 200 nm within the scratch only.

POSS-Kapton[®] samples containing 0 wt %, 3.5 wt % and 7.0 wt % Si₈O₁₁ were exposed to AO from a hyperthermal O-atom beam while the sample temperature was held at 25 °C, 100 °C, 150 °C, 220 °C, and 300 °C. Studies of the exposed samples showed that although the erosion of POSS-PIs increased with temperature, they erode significantly less than their no-POSS analogous at elevated temperatures.

Physical property characterization of POSS-PIs exposed to AO, and samples flown in LEO on the Materials International Space Station Experiment (MISSE), evidence that POSS-PIs are a viable Kapton[®] replacement material.

INTRODUCTION

Kapton[®] polyimide is used extensively on spacecraft in flexible substrates for lightweight, high-power solar arrays because of its inherent strength, temperature stability, excellent insulation properties, UV stability and IR transparency. It is also used in conjunction with Teflon FEP in multilayer insulation blankets for thermal control insulation because of its superior optical properties, including low solar absorptance. In these multilayer insulation blankets, aluminium (or gold) is typically applied to Kapton[®] due to its low emissivity.[1]

It has been well established through space flight experiments and ground-based simulations of atomic oxygen in LEO that polymeric materials undergo severe degradation as a result of the aggressive environment encountered in LEO.[2-10] In this high vacuum environment, materials are subjected to solar radiation, thermal cycling which can range from -50 °C to 150 °C, bombardment by low and high-energy charged particles, as well as high incident fluxes of AO.[11] These harsh conditions necessitate the design of space-survivable materials.

Atomic oxygen in LEO impacts materials with a collision energy of 4.5-6 eV. [12-14] This O-atom translational energy is enough to overcome many reaction barriers and facilitates the degradation of Kapton[®]. The silicon-oxygen bond energy is 8 eV, and this bond is intact after AO exposure. For this reason, Kapton[®] is typically coated with silica to impart resistance to AO. Imperfections in the silica layer created during the deposition process, or during flight, lead to uncoated Kapton[®] which erodes readily in the presence of AO. Cracked or damaged silica (or aluminium) coatings on Kapton[®] can lead to the trapping of reactive AO. Monte Carlo simulations by K. de Groh et al, have shown that this reactive AO can ricochet in trapped spaces before reacting causing an undercutting effect which can burrow out cavities in the Kapton[®] polymer matrix thereby causing increased material erosion.[2]

The nanodispersion of Si and O throughout the polyimide polymer matrix leads to the formation of a protective silica layer on the polyimide surface when the material reacts with AO. Our data indicates that upon AO exposure, the organic material in the polymer surface erodes, while the atomic oxygen reacts with the nanodispersed POSS to form a silica layer. Therefore, when POSS is copolymerized to form POSS-PI, it imparts remarkable AO resistance, and does so with minor effects in the storage modulus, glass transition temperature, and coefficient of thermal expansion.[15]

Evidence for the formation of a protective silica layer on the surface of POSS-PIs upon exposure to AO was found in X-Ray Photoelectron Spectroscopy (XPS) studies of POSS-PIs flown on MISSE1, and in separate studies of POSS-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton H[®], SiO₂ coated Kapton HN[®], and 8.75 weight % Si₈O₁₁ cage “main-chain” POSS-polyimide (8.75 wt % Si₈O₁₁ MC-POSS-PI), these materials were exposed to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study

indicate that a silica layer is formed upon exposure of POSS-PIs to AO, and after scratching this layer, a new silica layer forms in the scratched area during AO exposure. Physical property characterizations and the effects of an approximately four year flight of POSS-PIs on the International Space Station will be presented.

EXPERIMENTAL

Synthesis of POSS-Polyimide Copolymers

Polyimides with the same chemical formula as Kapton[®] were synthesized by condensation polymerization of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N'-dimethylacetamide (DMAc) solvent [15, 16]. A POSS dianiline monomer (Figure 1) with two aniline pendant groups and eight cyclopentyl pendant groups was synthesized using a procedure described by Prof. Frank Feher in 2003 [17]. Using this monomer, POSS-polyimide random copolymers were synthesized as shown in Figure 1 with POSS monomer loadings corresponding to 0, 5, 10, 20, and 25 wt%, which correspond to Si₈O₁₁ cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %. ODA was recrystallized from toluene:DMF in a 10:1 vol:vol solution, and PMDA was recrystallized from dioxane. ODA, PMDA, and POSS were stored under nitrogen in amber glass jars. For all the polymerizations the mole ratio of diamine (ODA + POSS) to dianhydride (PMDA) was 1:1. In a glove box nitrogen atmosphere, POSS dianiline and ODA were combined in a 50 ml round bottom flask equipped with a stir bar. PMDA was weighed into a separate 25 ml flask followed by addition of 2 ml DMAc to form a slurry. The PMDA/DMAc slurry was added drop-wise via a Hamilton[®] gas-tight syringe to the stirring ODA/POSS solution. DMAc was added to PMDA for continued addition and this was repeated until all PMDA was added, with the final aliquots in solution form. A viscous POSS/PMDA/ODA poly(amic acid) solution resulted and was diluted to a total of 20 ml with DMAc and was stirred overnight under nitrogen.

"Side-chain"-POSS (SC-POSS) monomer was synthesized by Wright, et al. [18] from which 3.5, 7.0 wt % Si₈O₁₂ cage SC-POSS-PIs were synthesized in the same manner as described above. All poly(amic acids) were cast onto level, ethanol washed and oven dried, glass plates and cured under nitrogen at 80 °C for four hours, 120 °C for 1 hour, 200 °C for 1 hour, and 300 °C for 1 hour. The resultant POSS-PIs were readily removed from the glass by lifting a corner with a razor blade under de-ionized water.

Exposure of POSS-Polyimides to Low Earth Orbit

POSS-PIs containing 0, 1.75, and 3.5 wt % Si₈O₁₁, were flown in LEO at about 500km on the International Space Station for nearly 4 years as part of the Materials International Space Station Experiment 1 (MISSE1). The samples were exposed to all aspects of the LEO environment including AO and UV light. The outer ring of the circular samples was covered in space by the sample holder top plate and was not exposed to the space environment during flight. The step height difference between this masked outer ring and the neighbouring exposed sample area was measured in twelve places around the circular sample by profilometry. The surface atomic composition of the samples was also determined by XPS.

AO Exposure of POSS-Polyimides

Ground based POSS-PI sample exposures were performed with a pulsed beam, operating at a repetition rate of 2 Hz and containing hyperthermal atoms that were generated with the use of a laser-detonation source [19-22]. The hyperthermal beam contains neutral atomic and molecular oxygen, with an ionic component of 0.01%. The mole fraction of atomic oxygen in the beam was above 70 % and, for some exposures, above 90 %. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve AO exposed and $1.7 \pm 0.1 \times 10^{15}$ O atoms cm^{-2} , and the mean translational O-atom energy was 4.9-5.0 eV.

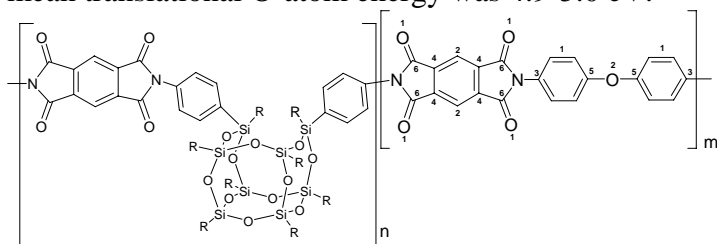


Figure 1. The structure of MC-POSS-Polyimide. R = cyclopentyl.

Surface Characterization of Scratched POSS-Polyimides

Samples were exposed to a hyperthermal O-atom beam as described previously. All samples in this work were handled in ambient air after exposure prior to etch depth, surface topography, and surface chemistry measurements.[23] To evaluate the effects of AO and temperature on samples, etch depths were determined by surface profilometry. These measurements were obtained with the use of a Dektak³ (Veeco Metrology Group, Santa Barbara, CA) surface profilometer. Scan lengths ranged from two to four microns, and scan speeds were slow to medium. The etched-mesh screens used to cover the samples had a wire thickness of 100 μm , with approximately square open areas that were 500 μm wide. Average step heights for the masked samples were obtained from 30 different step height measurements on each sample

Multiple samples of Kapton H[®], 8.75 % Si_8O_{11} MC-POSS PI, and silica-coated Kapton HN[®] (provided by Astral Technology Unlimited, Inc. Lot No. 00625-007, with a 130 nm SiO_2 coating) were exposed to hyperthermal AO. The beam was produced by a laser detonation source operating at 2 Hz, and previously described. [23] The sample mount was 40 cm from the source. Three samples of each type were exposed to 100k pulses of the beam, along with a Kapton H[®] standard. One sample of each material was covered by a screen, as described above, to provide exposed and protected areas for etch depth measurements. After the first exposure, the samples were removed from the chamber. The etch depths of the screened samples were measured. A set of unscreened samples underwent surface morphology measurements. The third set of samples was scratched. For each sample, one approximately 40 μm wide and 1 μm deep scratch was made with a diamond-tipped scribe, and two approximately 20 μm wide and 1 μm deep scratches were made with a razor blade. All scratches were measured by profilometry

(with a 5 μ m radius probe tip) in several places. Screens were placed over the scratched samples and these samples were exposed to additional 100k shots of the hyperthermal AO beam. After removal of the samples from the chamber, profilometry was used to measure step height differences between exposed and unexposed areas and to profile each scratch in AO exposed and unexposed areas.

XPS data was obtained with the use of non-monochromatized Mg K α radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Sample charging shifted the XPS lines to higher binding energies by 0.5 to 3 eV. In the present study, this shift was corrected by assuming that the binding energy of the lowest C(1s) component is 285.0 eV for the unexposed polyimide (0 wt% POSS) sample. (Note that the binding energy scale was calibrated with the use of an Ag(3d_{5/2}) line at 368.25 eV from another sample that underwent the same AO exposure as a reference.)

Scanning electron microscopy (SEM) was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector. Elemental mapping was performed using energy dissipation X-ray analysis with IXRF Systems analysis software.

Physical Properties Characterization of POSS-Polyimides.

The cured films were cut into 3 x 20 mm rectangular samples for dynamic mechanical thermal analysis utilizing a DMTA V from TA Instruments. All polyimide samples were analyzed using a 5 °C/min temperature ramp from room temperature to 500 °C and a tensile geometry. Stress/strain tests were performed on all samples to identify the largest force in which the material exhibited an elastic deformation, thus limiting the pretension force used to test the samples. Strain sweeps were performed to ensure that the testing strain was within the linear viscoelastic region.

Measurements of the coefficient of thermal expansion (CTE) were taken on a thermo mechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment, in a nitrogen atmosphere. The cured films were cut into 15mm by 3mm samples, the force applied was 0.05N & 0.10 N, and the sample was heated at 5 °C/min. The CTE was calculated as $\alpha = (\Delta L \times K) / (L \times \Delta T)$ where L = length, K = a cell constant, T = temperature °C. Test variability was +/- 2.306 ppm/ °C based on five Kapton H[®] tests.

The Effect of Temperature on The Erosion of POSS-Polyimides by a Hyperthermal O-Atom Beam.

The erosion of 0 wt %, 3.5 wt % and 7.0 wt % Si₈O₁₁ POSS-polyimides exposed to a hyperthermal O-atom beam has been studied at 25 °C, 100 °C, 150 °C, 220 °C, and 300 °C. Two samples of each type of material were exposed simultaneously. One of each sample type was covered with a screen to create exposed and unexposed areas so that the erosion depth could be determined by profilometry, while the other sample per each type was not covered by a screen during exposure. Each exposure was to 50,000 pulses of the hyperthermal O-atom beam, with a 40 cm distance between the conical source nozzle and the samples, and included a “screened” Kapton H[®] reference sample. The nominal O-atom translational energy of each exposure was 5.2 eV, and the O/O₂ ratio in the beam was 0.65:0.35. For the 25 °C exposure, the films (which were not cast on substrates) were

placed in the sample holder. For the higher temperature exposures, the films were cast on germanium discs that were in contact with a controlled heating block during the exposures, and were equilibrated to the desired temperature.

RESULTS AND DISCUSSION

MC-POSS-PI (POSS “R” group is cyclopentyl) films were etched by exposure to a hyperthermal O-atom beam. As described previously [24], the beam was produced by combining oxygen with a 7 Joules per pulse CO₂ laser source. The resultant O-atom beam consists predominantly of fast neutrals, with a very small ionic fraction ($<10^4$). Kinetic energies of the fast O-atoms in the beam can range from 2 to 15 eV, with the average being about 5.2 eV. A stainless steel screen was placed over the sample in order to selectively erode only certain portions of the samples. The difference in etch depth between the eroded and protected areas of the samples, measured using stylus surface profilometry, made it possible to calculate an AO reaction efficiency (R_e) or erosion rate of the material for a given flux.[2]

The AO reaction efficiency of Kapton H[®] was used to calculate the Kapton[®] equivalent fluence and erosion yields of each sample exposure. For various exposures, the step heights (or etch depths) of POSS-PI films were plotted as a function of the step height of the Kapton H[®] film. [25, 26] The derivative functions indicated that the 3.5 and 7.0 wt % Si₈O₁₁ POSS polyimide films reached erosion rates of 3.7 and 0.98%, respectively, of the erosion rate for Kapton H[®] after 395,000 beam pulses (8.47×10^{20} atoms cm⁻²). [9, 10] 8.75 wt% Si₈O₁₁ POSS-PI samples had an erosion rate that was 0.3 percent of the erosion rate for Kapton H[®], and 1/3 of 7.0 wt % POSS-PI at a fluence of 8.5×10^{20} atoms cm⁻². These results support the formation of a passivating silica layer that is formed as a result of the nano-dispersed POSS moieties reacting with AO.

A “self-passivation test” was carried out to better assess the protective silica layer formation witnessed by XPS of POSS-PIs. Kapton H[®], SiO₂ coated Kapton HN[®], and 8.75 wt % Si₈O₁₁ MC-POSS-PI were exposed to equivalent AO fluences. The etch depth of the Kapton H[®] after the initial exposure was 7.0 ± 0.2 μm, indicating an O-atom fluence of 2.3×10^{20} O atoms cm⁻². This sample appeared significantly roughened after exposure. The etch depth of 0.26 ± 0.15 μm of the 8.75 wt % Si₈O₁₁ MC-POSS-PI film was difficult to measure since the overall etch depth was not much greater than the slight roughness caused by the exposure. For the SiO₂ coated Kapton HN[®] the etch depth was below the practical measurement limit of the profilometer and the sample surface appeared unaffected.

SEM images of Kapton H[®], SiO₂-coated Kapton HN[®], and 8.75 wt % Si₈O₁₁ MC-POSS-PI that were AO-exposed, scratched, and underwent a second exposure to 2.3×10^{20} O atoms cm⁻² are shown in Figure 2. Examples of profilometer traces of the scratches in AO-exposed and unexposed areas are shown in Figure 3. For the SEM image of Kapton H[®], the exposed region is in the left side of the image and has a more roughened surface with a deepened scratched area. The etch depth of the Kapton H[®] sample outside of the scratch was about 5.5 μm. The scratch was 20 μm wide and 1 μm deep unexposed and 1.4 μm deep relative to the neighboring eroded surface after the second exposure. The top of

the SiO₂-coated Kapton HN[®] image was exposed to AO and only had erosion in the scratched area with unaffected neighboring silica-coated Kapton HN[®], demonstrating the effects of damage to silica coatings on Kapton[®]. Here the unexposed scratch was 20 μm wide and 1 μm deep and the exposed scratch was 8 μm deep relative to the neighboring exposed surface, amounting to 7 μm of erosion in the scratch. 8.75 wt % Si₈O₁₁ MC-POSS-PI was exposed to AO in the darkened upper right area in Figure 2c. A difference in step height between exposed and unexposed unscratched areas of the 8.75 wt % Si₈O₁₁ MC-POSS-PI was < 200nm and is not visible by microscopy. In Figure 2c, the scratch was 35 μm wide and 1.4 μm deep unexposed and about 1.8 μm deep after AO exposure. This result indicates that 8.75 wt % Si₈O₁₁ MC-POSS-PI experienced 400 nm of erosion inside the scratch during AO exposure. In comparison, Kapton H[®] eroded about 5 μm inside and outside the scratch, plus Kapton H[®] eroded an additional 0.400 μm in the scratch during exposure. In all instances, the scratched regions apparently eroded slightly more than the unscratched exposed areas. This may be explained by the undercutting effect described above where the O-atoms are focused deeper into the polymer matrix by scattering from the sidewalls of the scratches. These results are summarized in Table 1.

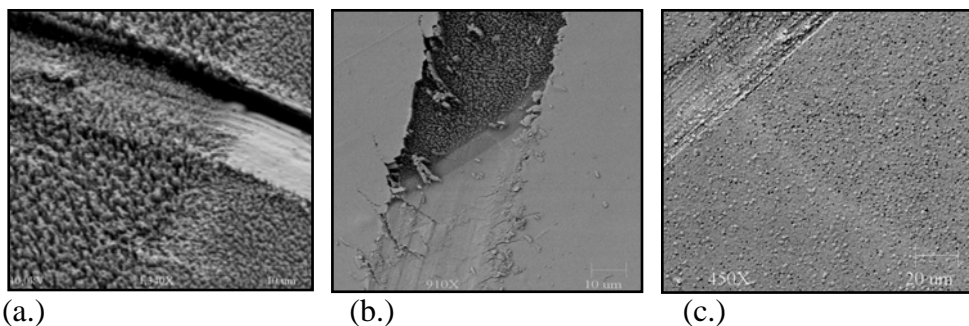


Figure 2. SEM images of results from a self-passivation experiment. (a.) Kapton H[®], (b.) SiO₂ coated Kapton HN[®] (Provided by Astral Industries Inc.), and (c.) 8.75 wt % Si₈O₁₁ cage MC-POSS-PI. Samples were exposed to 2.3×10^{20} atoms/cm², scratched, covered by a wire screen and exposed again to 2.3×10^{20} atoms/cm². The area covered by the wire screen was (a.) the right side, (b.) the bottom portion, and (c.) the left side.

Table 1. Self-Passivation Experiment Summary

Material	Kapton H [®]	SiO ₂ -coated Kapton HN [®] with Aluminum under-coating	8.75 wt % Si ₈ O ₁₁ MC-POSS PI
Erosion depth after 1st exposure.	5.5 μm	~ 0 μm	0.200 μm
Erosion depth outside of the scratch after 2nd exposure.	5 μm	~ 0 μm	~ 0 μm
Erosion depth inside of the scratch after 2nd exposure.	5 μm	7 μm	~ 0.400 μm

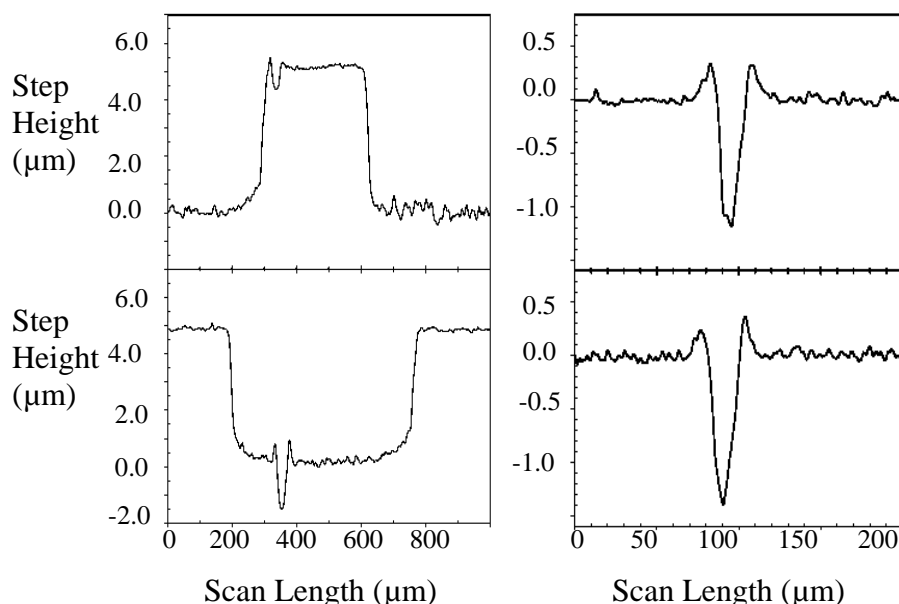


Figure 3. Profilometer traces of scratches in covered (top) and uncovered (bottom) areas of the Kapton H[®] (left) and 8.75 wt % Si₈O₁₁ MC-POSS-PI (right). The covered areas were exposed to 2.3×10^{20} oxygen atoms cm⁻², scratched, and covered with a stainless steel screen. The uncovered areas were exposed to 2.3×10^{20} oxygen atoms cm⁻², scratched, and again exposed to 2.3×10^{20} oxygen atoms cm⁻².

The results of the study of the effect of temperature on AO erosion of POSS-polyimides are given in Tables 2 and 3 below. The results in Table 1 show that polyimide and POSS-PIs experience increasing erosion with increasing temperature. It is interesting to note that the erosion of Kapton H[®] decreases at 300 °C which is the final cure temperature for Kapton[®] polyimide. For each temperature, the etch-depths of the POSS-PIs (Table 2) divided by the etch depth of Kapton H[®] are given in Table 3. The erosion of the 0 wt % POSS-PI exhibited the strongest temperature dependence, with the etch depth increasing by a factor of about 3.6 from 25 °C to 300 °C. The 3.5 wt % and 7.0 wt % Si₈O₁₁ POSS-PIs showed less temperature dependence in their erosion. The etch depths of these samples increase by factors of 2.2 and 2.4, respectively, with the increase from 25 °C to 300 °C, and with the uncertainty in the measurements, these factors might be considered the same.

Table 2. The etch depths for polyimide, 3.5 wt % and 7.0 wt % Si₈O₁₁ POSS-polyimides, and Kapton H[®] after exposure to a hyperthermal O-atom beam at five temperatures.

Temperature of the Sample	Polyimide (μm)	3.5 wt % Si ₈ O ₁₁ POSS-polyimide (μm)	7.0 wt % Si ₈ O ₁₁ POSS-polyimide (μm)	Kapton H [®] (μm)
300 °C	10.37 ± 0.47	1.24 ± 0.17	0.67 ± 0.16	3.14 ± 0.13
220 °C	7.47 ± 0.37	0.94 ± 0.21	0.78 ± 0.08	3.46 ± 0.20
150 °C	5.36 ± 0.23	1.02 ± 0.11	0.41 ± 0.07	3.59 ± 0.11

100 °C	4.09 ± 0.38	0.82 ± 0.07	0.43 ± 0.06	3.55 ± 0.11
25 °C	3.17 ± 0.24	0.63 ± 0.08	0.30 ± 0.08	3.50 ± 0.12

Table 3. The ratio of etch depths for polyimide, and 3.5 wt % and 7.0 wt % Si₈O₁₁ POSS-polyimides to Kapton H[®] after exposure to a hyperthermal O-atom beam at five temperatures.

Temperature of the Sample	Polyimide/ Kapton H [®] (μm)	3.5 wt % Si ₈ O ₁₁ POSS-polyimide/ Kapton H [®] (μm)	7.0 wt % Si ₈ O ₁₁ POSS-polyimide/ Kapton H [®] (μm)
300 °C	3.30 ± 0.20	0.40 ± 0.06	0.21 ± 0.05
220 °C	2.16 ± 0.16	0.27 ± 0.06	0.23 ± 0.03
150 °C	1.49 ± 0.08	0.28 ± 0.03	0.11 ± 0.02
100 °C	1.15 ± 0.11	0.23 ± 0.02	0.12 ± 0.02
25 °C	0.91 ± 0.08	0.18 ± 0.02	0.086 ± 0.02

The results show that although POSS-PIs have increased erosion with temperature, they do erode less than their no-POSS analogous at elevated temperatures. In most cases, except at 200 °C, a doubling of the POSS content from 3.5 wt % to 7.0 wt % Si₈O₁₁, causes the etch depth to decrease by about half. The O-atom fluences used in this study are at least half of those used in other work with these materials. It has been seen that at higher O-atom fluences, at room temperature, there is an increasing difference in the erosion of polyimide and POSS-PI. This is because the erosion of polyimide increases linearly with fluence while the erosion of POSS-polyimide increases by approximately the square root of the fluence. [25, 26] Hence, it is expected that the higher fluence exposures, at elevated temperatures, may reveal a more marked reduction in erosion yields for the POSS-polyimides compared to the erosion yields for the polyimide and Kapton H[®] films.

The physical properties of POSS-PIs were evaluated by DMTA at Edwards Air Force Research Laboratory and have been discussed previously.[15] The glass transition temperatures (T_g) were as follows: 420 °C for 0 % POSS-PI, 394 °C for 3.5 % Si₈O₁₁ MC-POSS-PI, 390 °C for 7 % Si₈O₁₁ MC-POSS-PI, 383 °C for 8.75 % Si₈O₁₁ MC-POSS-PI. The 7 % Si₈O₁₁ MC-POSS-PI exhibited a tan δ peak very similar in intensity and breadth to the 0 % POSS-PI peak, while the 3.5 and 8.75 wt % Si₈O₁₁ MC-POSS-PI tan δ peaks were slightly greater than half the height and of similar width to the 0 and 7 wt % POSS samples. This unique behavior of the 7 wt % Si₈O₁₁ MC-POSS-PI may be from similar chain packing to the 0 % POSS-PI sample. A side-chain POSS (SC-POSS) monomer has been synthesized by Wright et al. and was readily copolymerized to form POSS-PIs with POSS as a pendant group. In an AO exposure with a total fluence of 3.53×10^{20} O atomx/cm⁻², 7 % Si₈O₁₂ SC-POSS-PI had an erosion yield that was 3.3 % of Kapton H[®]. In a previous AO exposure study total fluence of 4.10×10^{20} O atoms/cm⁻², 7 % Si₈O₁₁ MC-POSS-PI had an erosion yield that was 3.8 % of Kapton H[®]. These results indicate that MC- and SC-POSS-PIs have approximately equal AO resistance. DMTA measurements taken at Michigan State University have shown that the T_g of 7 wt % Si₈O₁₂ SC-POSS-PI is 400 °C, and decreases to 378 °C after exposure to 2.3×10^{20} oxygen

atoms cm⁻². The tan δ peaks for this material were slightly more intense and broader than commercial Kapton H[®], but were not yet compared to 0 % POSS-PI. It is important to note that, due to instrumentation, the DMTA measurements taken at Michigan SU are consistently 20 °C less than those taken at Edwards AFB.

The sudden temperature changes experienced by materials in the LEO environment make the coefficient of thermal expansion (CTE) a highly important material property. In order for POSS-PIs to be a drop-in replacement for Kapton[®], it is necessary that the new material have predictable CTEs with similar values to Kapton[®]. The CTE values for several samples are shown in Table 4. The addition of POSS slightly increases the CTE, and a slight decrease is seen after exposure of the SC-POSS-PI to AO. Mismatches in the CTEs between polymeric materials and their coatings lead to cracks, crazing, and mechanical material failure. The CTE of fused silica is about 0.55(μm/m°C) [27, 28] and the CTE of the silica passivation layer formed on POSS-PIs in the presence of AO is expected to be close to silica in value. This mismatch between the silica passivation layer and the underlying POSS-PI is likely to cause cracks in the silica. The self-passivating properties of the POSS-PIs described above result in the formation of a silica passivation layer in the areas where cracks or damage have occurred, once again protecting the underlying POSS-PI.

Table 4. Coefficients of Thermal Expansion for POSS polyimide films.

Sample	*CTE (μm/m°C)*
Kapton H [®]	30.25
0% POSS-PI	33.11
7 % MC-POSS-PI	33.5
8.75 % MC-POSS-PI	35
7 % SC-POSS-PI	35.86
7 % cage SC-POSS-PI exposed AO [†] to	33.64

*Test variability based on 5 Kapton H[®] tests = ± 2.306 ppm/°C.

[†]2.3x10²⁰ oxygen atoms cm⁻²

MC-POSS-PI films were recently retrieved from the Materials International Space Station Experiment after being flown in LEO for 3.9 years on a sample holder that was exposed to all aspects (AO, UV) of the LEO environment. These films included a 0, 1.75, and 3.5 wt % Si₃O₁₁ MC-POSS-PIs. All films were adhered to an aluminum substrate before flight. The innermost portion of the circular samples experienced greater erosion than the portion furthest from the center of the samples. The outer portion neighbors the edges that were covered by an aluminum mask throughout the flight and remained unexposed to the space environment. The step heights from the unexposed (masked) area and the neighboring exposed outer portion of the sample were measured. It was found that a 32.55 \pm 0.87 μm thick polyimide film completely eroded. 1.75 % MC-POSS-PI showed some survival with a step height of 5.79 \pm 1.31 μm between the exposed outer portion and the masked area, although the inner portion of this sample completely eroded. 3.5 % MC-POSS-PI film remained throughout with a step height of 2.12 \pm 0.34 μm from the outer portion and the unexposed area, and an inner region that experienced greater erosion causing thinner areas of the film. It was determined by XPS

that the atomic percentages of the top 10 nm of the films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% Si₈O₁₁ MC-POSS-PI samples.

CONCLUSION

The incorporation of POSS nanostructures into polyimides has been shown to significantly extend the lifetime of these materials in LEO. Studies on the effect of a hyperthermal O-atom beam on POSS-PIs have shown the improved oxidation resistance imparted to polyimides by the addition of POSS. XPS data of both the AO-exposed and space-flown POSS-PI materials indicated that the improved oxidation resistance of these materials is due to a rapidly formed silica layer upon exposure of POSS-polymers to high incident fluxes of atomic oxygen.

A study of the response of scratched materials to AO showed that if a Kapton H[®] surface is scratched, the scratched material will erode at roughly the same rate as undamaged Kapton H[®]. A SiO₂ coating of 130 nm protected underlying polyimide from AO attack, but after the coating was compromised, the exposed polymer eroded (during AO exposure) at approximately the same rate that uncoated Kapton[®] eroded. The 8.75 wt % Si₈O₁₁ MC-POSS-PI experienced roughly 1 - 2 % the erosion yield of Kapton H[®] that was exposed to an equivalent amount of AO. This is presumably due to a silica layer formed on the surface of the material during AO exposure. When this layer was removed by a scratch, newly AO-exposed material had the same low erosion yield, indicating that a silica passivating layer formed in the scratched area.

It was found that the incorporation of POSS slightly reduces the glass transition temperature (T_g) of Kapton[®] polyimide, however, the T_g values of POSS-PIs are well above the temperatures experienced by materials in LEO. The CTE of POSS-PIs is similar to the CTE of commercial Kapton H[®]. A new SC-POSS monomer imparts about the same AO resistance to polyimides as the MC-POSS monomer. The modulus, T_g, and CTE of SC-POSS-PIs were determined before and after exposure to atomic oxygen, and are comparable to the values of these properties for Kapton H[®].

POSS-polyimide samples had flown on the International Space Station for nearly 4 years and showed space-survivability in LEO, with a film of the 3.5 wt % Si₈O₁₁ POSS-polyimide remaining.

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